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NUTRIENT DYNAMICS IN EUTROPHIC LAKES

EFFECTS OF RESUSPENSION, MACROPHYTES AND OXYGEN

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ACADEMIC DISSERTATION

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ABSTRACT

The dynamics of phosphorus (P) and nitrogen (N) were examined in two (shallow and deep) eutrophic lakes. The effects of resuspension and macrophytes as well as oxygen availability were determined, as was the role of natural nitrogen (N) removal (denitrification).

The effect of resuspension on the availability of N and P was examined in experimental columns in a shallow eutrophic lake. The release of soluble reactive P (SRP) from resuspended matter varied both seasonally and interannually, depending on the conditions in the lake. SRP release was most significant during periods of high primary production, probably due to pH-induced ligand-exchange reactions. The effect of resuspension on dissolved N was less clear, although resuspension also increased the concentrations of ammonium, nitrite and nitrate during some of the experiments. The studies also showed that strong resuspension decreases the total N to total P ratio in the water independently of the phase of the growing season.

The nutrient dynamics were further studied among two different macrophyte stands (submerged and floating-leaved macrophytes) and in the open water. The concentration of combined nitrate and nitrite N (NO_x^--N) decreased to the detection limit (< 2 $\mu g\ l^{-1}$) at all of the stations during summer. Among the submerged macrophytes, the NO_x^--N was depleted almost 2 months earlier than at the other stations, which restricted denitrification.

The rate of denitrification was measured with the isotope-pairing technique in both lakes. In the shallow lake, denitrification was measured at the location of the resuspension experiments as well as at the macrophyte stations and adjacent open-water area. Denitrification was mainly dependent on the availability of NO_x^--N and temperature, and also contributed to the changes observed in the total N to total P ratio in water during summer by removing substantial amounts of NO_x^--N from the water.

The effects of oxygen (O_2) availability were studied in a deeper, stratifying lake, where the deeps were treated with continuous or pulsed aeration, or with no aeration. The SRP release in the deeps was linked with the O_2 in the sediment and the SRP accumulated in the hypolimnion during the periods of anoxia. During the aeration pauses and pulses, the concentration of NO_x^--N decreased and increased respectively and the concentration of ammonium varied contrastingly. Continuous aeration prevented the ammonium from accumulating and provided NO_x^--N for denitrification to occur. Accordingly, denitrification showed higher rates during aeration. However, aeration also increased the temperature of the hypolimnion and thereby also the O_2 consumption.

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following publications, which are referred to in the text by their Roman numerals:

I Holmroos H., Niemistö J., Weckström K. and Horppila J. 2009. Seasonal variation of resuspension-mediated aerobic release of phosphorus. Boreal Environment Research 14, 937–946.

II Holmroos H., Hietanen S., Niemistö J. and Horppila J. 2012. Sediment resuspension and denitrification affect the nitrogen to phosphorus ratio of shallow lake waters. Fundamental and Applied Limnology 180, 193–205.

III Holmroos H., Horppila J., Niemistö J., Nurminen L. and Hietanen S. Dynamics of dissolved nutrients among different macrophyte stands in a shallow lake. Limnology (submitted).

IV Holmroos H., Horppila J., Laakso S., Niemistö J. and Hietanen S. The effects of aeration on nitrogen dynamics of a dimictic lake. (manuscript).

AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

I Holmroos had the main responsibility for writing the article. The study was designed and data collected jointly with Niemistö and the other authors. Niemistö was responsible for the original idea and data analysis.

II Holmroos designed the study and collected the data together with the co-authors. The data were analysed and the manuscript written by Holmroos. Holmroos was also the corresponding author of the article.

III Holmroos had the main responsibility for the original idea, study design and data collection. Holmroos also wrote the first version of the article and was the corresponding author.

IV Holmroos took part in the study design and data collection with the co-authors. Holmroos had the main responsibility for the data analysis and manuscript writing and was the corresponding author of the article.

ABBREVIATIONS

Al	aluminium
Anammox	anaerobic ammonium oxidation
C	carbon
Ca	calcium
CTD	conductivity, temperature, depth
D_{14}	denitrification rate
D_{15}	denitrification potential
DIN	dissolved inorganic nitrogen
DO	dissolved oxygen
DON	dissolved organic nitrogen
DNRA	dissimilatory nitrate reduction to ammonium
D_n	denitrification coupled to nitrification (%)
D_w	denitrification based on overlying water NOx- (%)
Fe	iron
FLOAT	floating leaved macrophyte station at Lake Kirkkojärvi
ICP	inductively coupled plasma
IPT	isotope pairing technique
LOI	loss on ignition
N	nitrogen
NH_4^+-N	ammonium nitrogen
NO_2^--N	nitrite nitrogen
NO_3^--N	nitrate nitrogen
NO_x^--N	combined nitrite and nitrate nitrogen
OH^-	hydroxide
OPEN	open-water station at Lake Kirkkojärvi
O_2	oxygen
P	phosphorus
PON	particulate organic nitrogen
PVI	percentage of volume infested
r-IPT	revised isotope-pairing technique
SRP	soluble reactive phosphorus
SS	suspended solids
SUB	submerged macrophyte station at Lake Kirkkojärvi
TFP	total fractionable phosphorus
TN	total nitrogen
TP	total phosphorus

1 INTRODUCTION

1.1 Phosphorus and nitrogen in eutrophic lakes

Phosphorus (P) and nitrogen (N) are the most important nutrients that sustain primary production in lakes, and the availability of these nutrients often determines the level of production (Healey & Hendzel 1979, Hecky & Kilham 1988). Eutrophication is a natural development of lakes, but due to human influence this progression can be accelerated. Lakes may receive external anthropogenic loading of nutrients e.g. via wastewaters and from agricultural runoffs. The rate of production is high in eutrophic lakes, while a large amount of organic material is also mineralized and oxygen (O_2) consumption is increased. This may lead to anoxia and affects not only benthic animals and fish, but also nutrient cycles (Correll 1998 with references, Ludsin et al. 2009, Foley et al. 2012).
Phosphorus is able to bind to particles and thereby is eventually buried in lake sediments. However, as conditions change, P may be released from the sediment and again become available for primary production. This process can be called internal loading, while external loading refers to nutrients coming from the catchment. The cycles of P and N are different, since the N cycle also includes N removal processes, such as denitrification. The various reactions that N and P confront in the sediment also influence the N:P ratio in the lake water. Due to denitrification, the N:P ratio is typically lower in the sediment than in the overlying water (Hamilton & Mitchell 1988). Resuspension brings settled material back to the water column and thereby decreases the N:P ratio in the lake water. The variation in the N:P ratio may result in changes in the phytoplankton composition of a lake, since the proportion of N_2-fixing cyanobacteria may increase with decreasing N:P ratio (Smith 1983, Hendzel et al. 1994).
Since eutrophication negatively affects the condition of a lake and its recreational value, restoration efforts are made. Restoration often attempts to influence the internal loading of a lake, e.g. by maintaining or restoring the O_2 conditions of lake sediment or by reducing sediment resuspension (Cooke et al. 2005).

1.2 Phosphorus dynamics in lakes

The P cycle is closely associated with the chemistry of iron (Fe). The oxidized form Fe(III) precipitates as hydroxides and binds P. However, under reducing conditions Fe(III) reduces to Fe(II) and soluble reactive phosphorus (SRP) is released (Mortimer 1941, 1942). Fe(III) begins to reduce in redox potentials of < 200 mV. Such reducing conditions in lake sediments

are often due to the oxidation of organic matter, and thereby microbes play an important role in P release (Roden & Edmonds 1997). The availability of O_2 markedly affects the redox-related P release, but when the entire water column is oxic, especially in shallow areas, the importance of aerobic P release increases. Aerobic P release is often based on specific ligand-exchange reactions that occur on Fe or aluminium (Al) oxides (Hingston et al. 1967, Lijklema 1980, Koski-Vähälä & Hartikainen 2001). For example, hydroxide (OH^-) and silicate compete with phosphate for sorption sites on particles and P release occurs (Andersen 1975, Tallberg & Koski-Vähälä 2001).

Nutrients can be released into the sediment porewater and diffused into the water column above the sediment. However, resuspension, a mechanism that transports already settled material back to the water column, is often the most important mechanism of internal loading (Kristensen et al. 1992, Søndergaard et al. 1992). Resuspension is usually wind-induced but fish or benthic animals may also cause resuspension via bioturbation. The resuspension rates of P are also regulated by macrophytes that both decrease the water currents above the sediment and affect the nutrient concentrations in the sediment (Horppila & Nurminen 2005). Macrophytes take nutrients for their growth from the sediment or from water (Best & Mantai 1978, Ciurli et al. 2009) and also release nutrients into their environment (Lee & McNaughton 2004, Longhi et al. 2008), thus affecting nutrient cycling during the growing season.

Resuspension increases the concentration of suspended solids (SS) in water and in shallow lakes may account for most of the gross sedimentation (Evans 1994, Weyhenmeyer 1998). The effect of resuspension on internal P loading is well recorded (Reddy et al. 1996, Cyr et al. 2009, Gerhardt et al. 2010). Furthermore, the aerobic release of SRP from the sediment may account for most of the total P (TP) load of a shallow lake (Boström et al. 1988b, Jensen & Andersen 1992, Rydin & Brunberg 1998). The effect of resuspension on P is, however, not straightforward; resuspended particles may also adsorb SRP or have no effect on it (Boström et al. 1988b, Søndergaard et al. 1992, Horppila & Nurminen 2001). The effect of resuspension on P release is dependent on e.g. nutrient concentrations in the water and in the sediment, pH and concentration of O_2 (Koski-Vähälä & Hartikainen 2000).

1.3 Nitrogen dynamics in lakes

Although the limiting nutrient in lakes is usually P (Schindler 1977), the production may also be N-limited part of the year. The microbe-mediated N cycle is also crucial to productivity in determining in which form N is available. Atmospheric N_2 gas dissolves into the water but is not usually available for the primary producers that use dissolved inorganic nitrogen

(DIN) forms in their growth: ammonium N (NH_4^+-N), nitrite N (NO_2^--N) and nitrate N (NO_3^--N). N_2 fixation is an energy-demanding process that breaks the triple bond between the N atoms and reduces N_2 to NH_4^+-N. To fix N_2 biologically, nitrogenase enzyme is needed. The potential for N_2 fixation is found among bacteria and archaea (Dugdale & Dugdale 1962, Murray & Zinder 1984). Biologically fixed N, as well as DIN, are used by primary producers and converted to organic forms. Organic N is eventually used in mineralization and nitrification processes that return it to DIN (Fig. 1). In addition to mineralization processes, DIN ends up in bodies of water, e.g. from sewage loading, agriculture that uses synthetic N fertilizers or atmospheric deposition.

In addition to growth of primary producers, DIN may also be used in energy metabolism of microbes (Fig. 1). Such processes include nitrification, denitrification, dissimilatory nitrate reduction to ammonium (DNRA) and anaerobic ammonium oxidation (anammox). Nitrification is an aerobic process, but denitrification, anammox and DNRA occur under anaerobic conditions. Denitrification and anammox are regarded as N-removal processes, since they convert DIN to N_2, which is not readily available for living organisms apart from those capable of biological N_2 fixation.

In anammox, NH_4^+-N and NO_2^--N are combined into N_2 and in denitrification NO_2^--N or NO_3^--N (NO_x^--N) is reduced to N_2 and N_2O. Denitrification is common among facultative anaerobic microbes that use NO_x^--N in their respiration when O_2 is not available (Knowles 1982). Since denitrification uses NO_x^--N that is provided by aerobic nitrification, it often occurs at the interface of the aerobic and anaerobic environments (Seitzinger et al. 2006), such as the surface sediment of lakes. Anammox has also been observed in some permanently stratified lakes, although it has been studied more in marine and brackish environments (Dalsgaard et al. 2005, Schubert et al. 2006, Hietanen 2007, Hietanen & Kuparinen 2008, Hamersley et al. 2009).

The DNRA process competes with denitrification for substrate, but since the end product of DNRA is NH_4^+-N, no DIN removal occurs. DNRA is effective in competition with denitrification, especially in sediments with high organic content (Kaspar et al. 1988, Gilbert et al. 1997, Burgin & Hamilton 2007) and in lakes denitrification rather than DNRA usually accounts for the reduction of NO_x^--N (Tiedje et al. 1982, Nizzoli et al. 2010). However, the processes and relationships between denitrification and DNRA are not fully understood and the knowledge of DNRA in lakes is inadequate.

Sediment resuspension also affects the N cycle in lakes, e.g. by transporting organic material back to the water column (Blackburn 1997). Unlike SRP, NO_x^--N does not sorb to sediment and NH_4^+-N sorbs only with weak electrostatic bonds. Therefore, the direct effect of resuspension on DIN is mainly restricted to transport of porewater to the water column (Corbett 2010). However, resuspension may also have pronounced effects on DIN

dynamics, since it aerates the sediment surface and thereby promotes aerobic mineralization and nitrification.

In the littoral zone, macrophyte stands also affect the N cycle. Macrophytes compete with microbes for DIN, but they also provide organic carbon (C) for heterotrophic processes, and during decay organic N is returned for mineralization. As a heterotrophic process, denitrification shows higher rates among macrophytes than in bare sediments (Forshay & Dodson 2011). Macrophytes also provide O_2 into the sediment and create microenvironments for coupled nitrification-denitrification (D_n) (Kufel & Kufel 2002). Although denitrification occurs when O_2 is depleted, it uses oxidized N forms as a substrate and thereby is indirectly dependent on the O_2 availability. On the other hand, dense macrophyte stands and large amounts of organic material in the sediments may suppress the positive effects of macrophytes on O_2 conditions in the sediment (Caffrey et al. 1993, Boros et al. 2011).

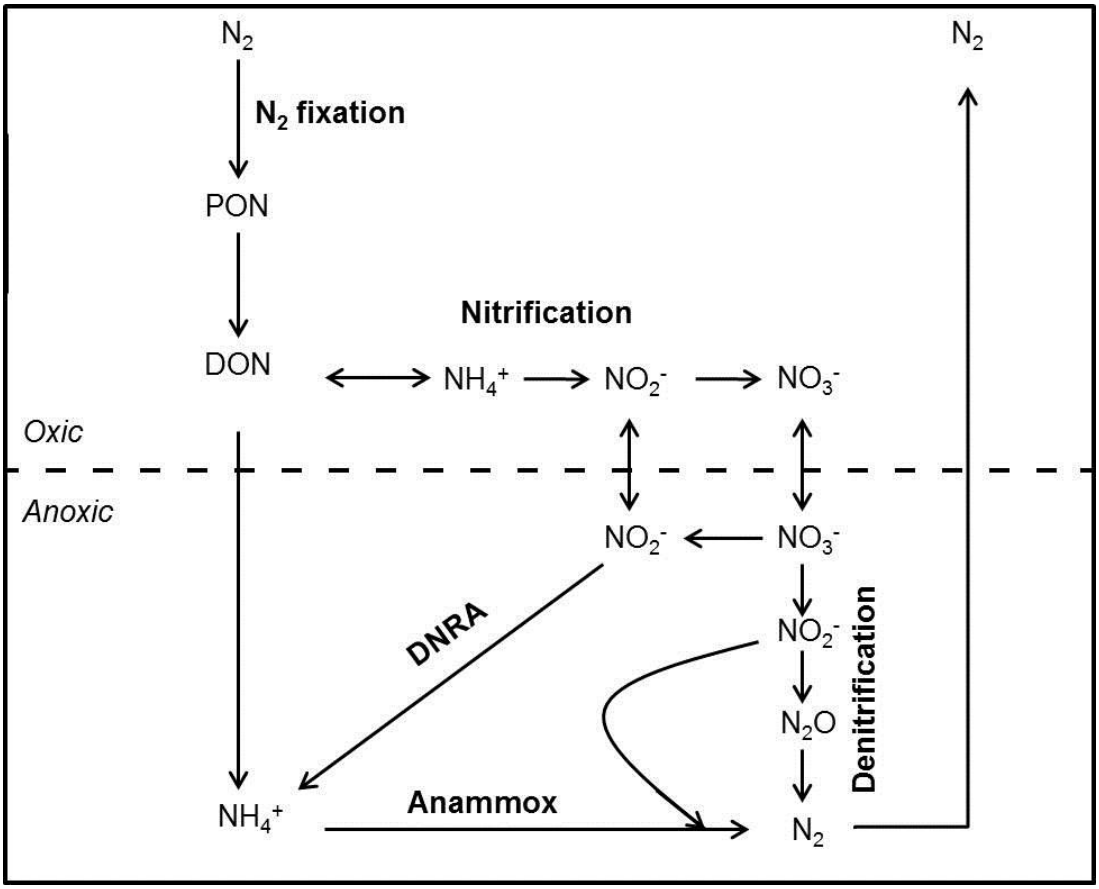

Figure 1. Simplified nitrogen cycle. PON = particulate organic nitrogen, DON = dissolved organic nitrogen, DNRA = dissimilatory nitrate reduction to ammonium, anammox = anaerobic ammonium oxidation.

1.4 Aims of the study

The aim of this thesis was to clarify the diverse dynamics of N and P in eutrophic lakes (Fig. 2). Since resuspension is the main process of internal loading in shallow lakes, its effects on aerobic P release and adsorption were experimentally studied. Aerobic P release is often linked to specific ligand-exchange reactions and the aim of the first study was to elucidate the effect of resuspension on SRP release under in situ conditions during high pH caused by algal blooms. We hypothesized that the effect of resuspension on aerobic SRP release would be more pronounced during intensive primary production in summer (**I**).

The experiments were further extended to examine the effect of resuspension on seasonal changes in the total nitrogen:total phosphorus (TN:TP) ratio and on DIN in water. The aim of the second study was to determine how resuspension affects the fractions of DIN. We hypothesized that since the amount of DIN in the sediment is low, the effect of resuspension would be more pronounced on concentrations of total nutrients and SRP than on DIN. We further hypothesized that strong resuspension would decrease the TN:TP ratio, regardless of the phase of the open-water season (**II**).

The nutrient dynamics were also studied among various macrophyte stands, since in a shallow lake a large percentage of the lake area may be covered with macrophytes. We hypothesized that the stands of the submerged macrophytes would more strongly affect the concentration of DIN and SRP than stands of the floating-leaved plants (**III**).

The rates of denitrification were studied during the open-water season in the shallow eutrophic lake: first at the open-water site of the resuspension experiments (**II**) and during the following open-water season also at the macrophyte stations (**III**). In relation to the resuspension experiments, we hypothesized that denitrification would contribute to the decrease in the water TN:TP ratio by decreasing the concentration of NO_x^--N in the water and sediment (**II**). We expected that denitrification would have higher rates at the macrophyte stations than at the open-water station (**III**). We likewise expected that the sediments among the macrophytes would have a higher organic content that would increase mineralization and decrease O_2 penetration, thereby enhancing denitrification (**III**).

The availability of O_2 and its effects on nutrient concentrations were further studied in a deeper stratifying lake (**IV**). The aim was to clarify whether artificial aeration is able to improve nitrification and prevent anaerobic P release. We hypothesized that in the artificially aerated deeps NO_x^--N would remain available in the water and consequently the denitrification rates would be higher. We also hypothesized that pulsed aeration would increase the hypolimnetic water temperature less than continuously operated artificial aeration (**IV**).

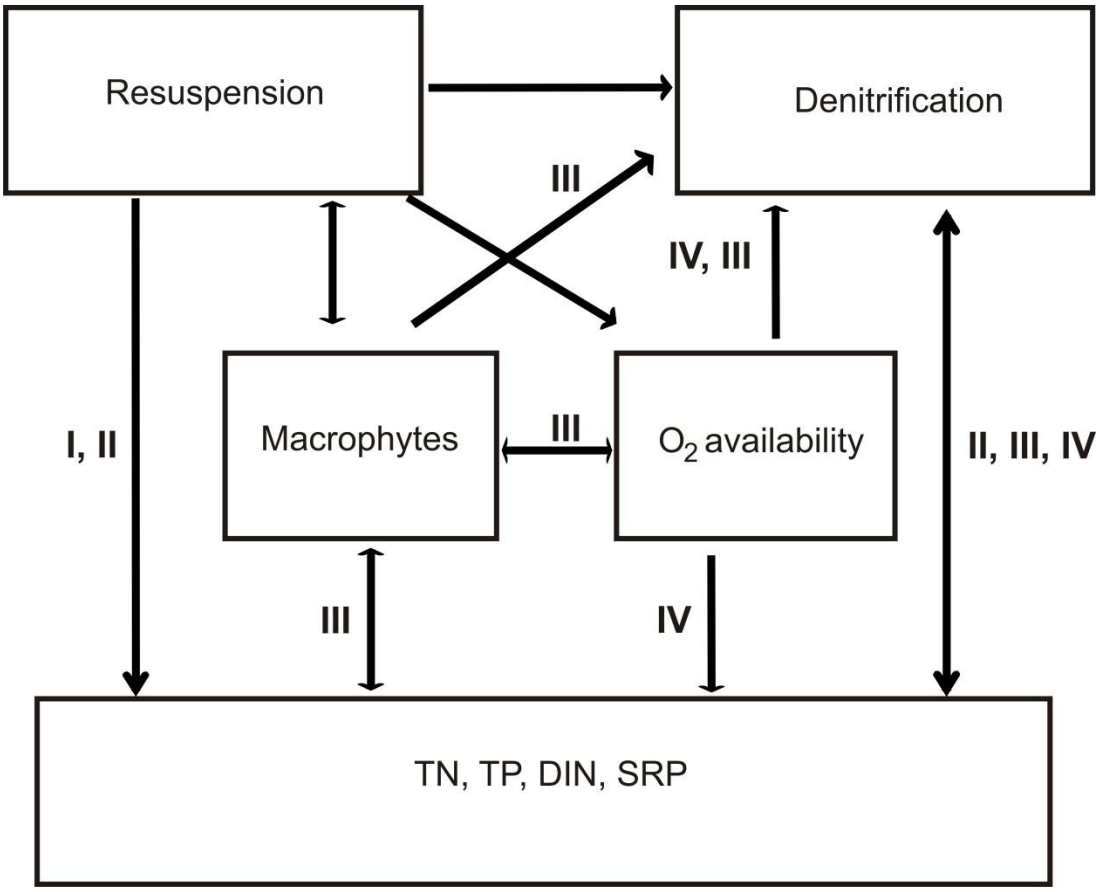

Figure 2. Schematic summary of the links between the various studies.

2 MATERIALS AND METHODS

2.1 Study lakes

2.1.1 Lake Kirkkojärvi (I–III)

Lake Kirkkojärvi is a basin of Lake Hiidenvesi (60°24' N, 24°18' E, 30.3 km^2), situated in southern Finland (Fig. 3). A total of 17% of the catchment area (935 km^2) of Lake Hiidenvesi is agricultural land and consequently the lake is exposed to heavy external loading. Lake Hiidenvesi has confronted anthropogenic eutrophication for decades (Harjula 1970) and in spite of restoration efforts it continues to suffer from cyanobacterial blooms (Tallberg et al. 1999, Hyytiäinen 2008). Lake Kirkkojärvi is the most eutrophic basin of Lake Hiidenvesi, with a summertime average TP concentration of 88 μg l^{-1} and TN concentration of 1250 μg l^{-1} (Horppila 2005). Lake Kirkkojärvi was chosen as a study area, since the basin (1.6 km^2) is shallow (mean depth 1.1 m, maximum depth 3.5 m) and frequently susceptible to resuspension. Due to continuous mixing, Lake Kirkkojärvi does not reach permanent thermal stratification and the entire body of water remains oxic throughout the open-water season.

2.1.2 Enonselkä basin of Lake Vesijärvi (IV)

The Enonselkä basin (61°01' N, 25°35' E, 26 km^2, mean depth 6.8 m, maximum depth 33 m, Fig. 3) is one of the four basins of Lake Vesijärvi, also situated in southern Finland. Large parts of the Enonselkä basin are shallow, but the deeper parts (18% of the water area) stratify thermally during summer and the thermocline lies at approximately 10 m. The catchment area of Lake Vesijärvi is 515 km^2 (23% fields). A significant part of the inflow is groundwater (Kuusisto 2010). This lake has also suffered from anthropogenic eutrophication, the lake received sewage discharge for 60 y from the city of Lahti, situated on the southern shore of the Enonselkä basin. Since 1976, the sewage load has been diverted and the water quality of Lake Vesijärvi has been improved in several consecutive restoration projects (Keto & Sammalkorpi 1988, Keto et al. 2005). Currently, the deeps of the Enonselkä basin are artificially aerated. The average summertime concentration of TP at the Lankiluoto Deep of the Enonselkä basin is 120 μg l^{-1} in the hypolimnion and 30 μg l^{-1} in the epilimnion. The average concentrations of TN are 1300 and 500 μg l^{-1}, respectively (Finnish Environment Institute 2012).

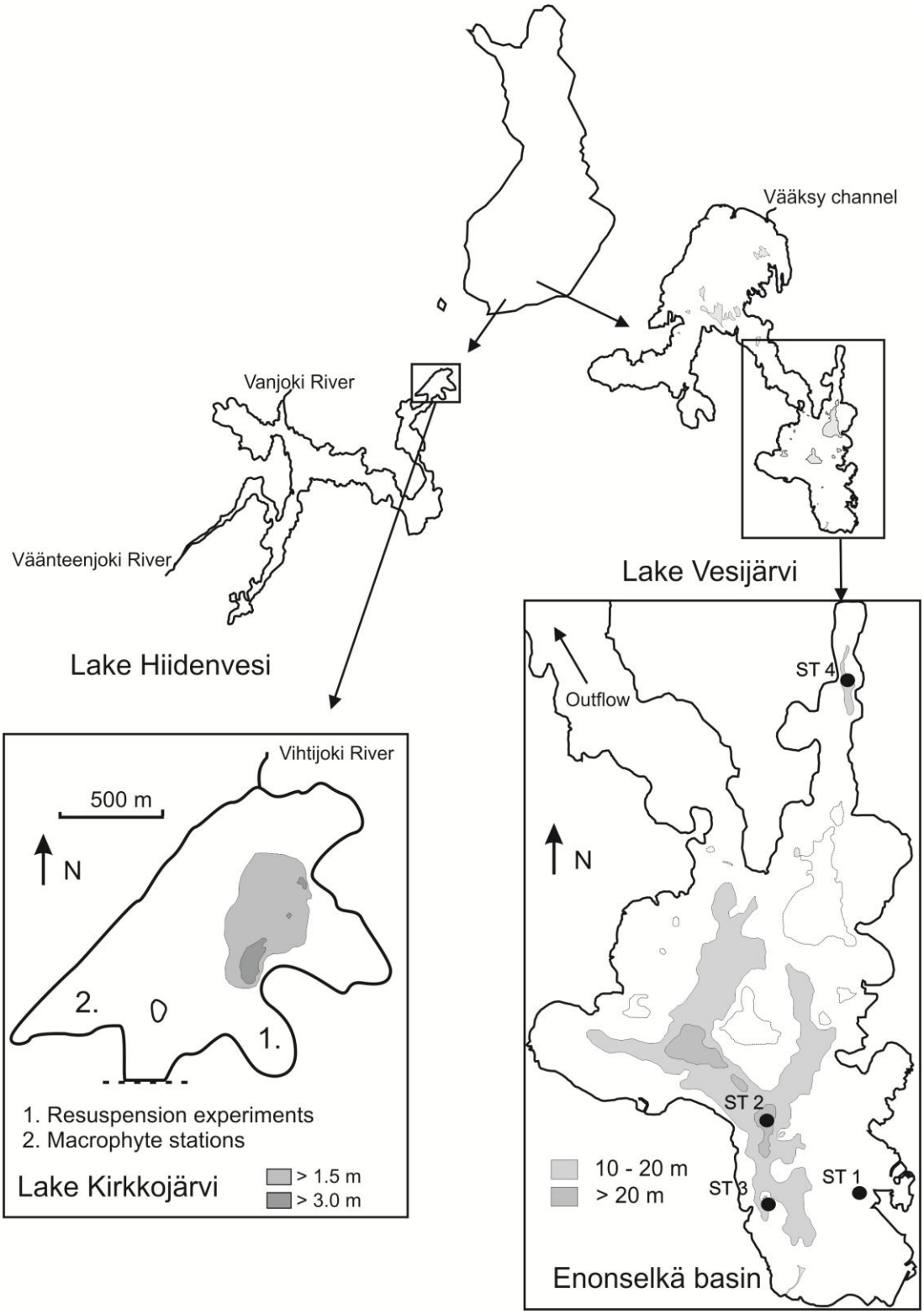

Figure 3. Study lakes and stations.

2.2 Water- and sediment-quality variables (I–IV)

Temperature, concentration and saturation of dissolved O_2, turbidity and pH were measured from the water columns at the study locations, using a conductivity-temperature-depth (CTD) sonde (YSI 6600V2; YSI Inc., Yellow Springs, OH, USA) (**I–IV**). In the Enonselkä basin of Lake Vesijärvi, daily monitoring data of temperature and concentration of O_2 in the water 1 m above the sediment was also available (monitored by the City of Lahti and Vesijärvi Foundation with automatic sensors) (**IV**). For the analysis of nutrients, water samples were collected with a Limnos tube sampler with a volume of 2.8 l (Limnos Ltd., Turku, Finland). TP and TN concentrations were determined spectrophotometrically after digestion or oxidation with peroxodisulphate (Koroleff 1979). The water samples for dissolved nutrients (SRP, NO_x^--N, NH_4^+-N) were immediately filtered in the field through polyethersulphone membrane syringe filters (pore size 0.2 µm; VWR International, Radnor, PA, USA). The concentrations of dissolved nutrients were also spectrophotometrically analysed according to the methods of Murphy & Riley (1962), Grasshoff et al. (1983) and Solorzano (1969), respectively. The nutrient analyses were done with a Lachat autoanalyser (QuickChem Series 8000; Lachat Instruments (Hach Company), Loveland, CO, USA). The concentration of chlorophyll *a* was measured spectrophotometrically after filtration on GF/C filters (Whatman, nominal pore size 1.2 µm; Whatman plc, Maidstone, Kent, UK) and extraction with ethanol (**I–III**).

The sediment samples were collected with an HTH corer (Renberg & Hansson 2008) (**I–IV**) and a Limnos sediment corer (**IV**). The loss on ignition (LOI) representing the organic content of the surface sediment (1 cm), was measured by combustion for 2 h at 550 °C (**I–III**). The O_2 penetration depth of the sediment was measured with a Unisense Picoammeter PA2000 and a Unisense OX100 microelectrode (vertical resolution 200 µm; Unisense A/S, Aarhus, Denmark) (**III**).

The various P pools of the surface sediment (1 cm) were determined twice at the location of the resuspension experiments in 2007 to define the processes of aerobic P release (**I**). The fractionation of the TP was performed by the method of Chang & Jackson (1957) (modified by Hartikainen 1979). This fractionation separates four different P pools: labile P, aluminium-bound P (Al-P), iron-bound P (Fe-P) and calcium-bound P (Ca-P).

2.3 Denitrification measurements (II–IV)

Denitrification rates (D_{14}) were measured from intact sediment cores with the isotope-pairing technique (IPT) (Nielsen 1992) (**III**) or with revised IPT (r-IPT) (Nielsen 1992, Risgaard-Petersen et al. 2003, 2004) (**II, IV**). In the IPT, samples are incubated with ^{15}N-labelled NO_3^- and the measure of

labelled N_2 is used to also calculate the formation of unlabelled N_2 (D_{14}), assuming random isotope pairing of labelled and unlabelled NO_3^-. The denitrification potentials (D_{15} values) were also measured as the slope of produced ^{15}N against incubation concentrations of $^{15}NO_3^-$-N (**II, IV**). The samples for the measurements were collected with HTH and Limnos corers and the nutrient concentrations were analysed from the water above the sediment by the methods described earlier (in chapter 2.2). The porosity of the sediment was analysed from 2 ml of homogenized sediment that was collected in a manner similar to that of the samples for denitrification measurements. The D_{14} values were measured three times in 2009 (**II**), four times in 2010 (**III**) and five or six times (depending on the station) in 2011 (**IV**).

2.4 Setup of the resuspension studies (I, II)

The resuspension experiments were conducted in experimental columns in Lake Kirkkojärvi (Fig. 1). Open columns (Ø 18.5 cm) were placed on the bottom of the lake so that the other end of the column reached the surface. The water depth at the experiment location was 1 m. In total, six columns were used, three of which were control units, while three received the resuspension treatment. In the treated columns, resuspension was induced with a piston and the strength of resuspension was evaluated by measuring the water turbidity. Linear regression between the turbidity and concentration of SS was quantified (SS = 1.5515 x turbidity - 4.7178, R^2 = 0.9883, p < 0.0001, $F_{1,24}$ = 1942.84) and the resuspension treatment was aimed at being intensive enough to transport all of the resuspendable material to the water column. After the resuspension treatment, the concentration of SS in the treated columns was 160–360 mg l^{-1}, a level observed in shallow lakes (Hamilton & Mitchell 1996, James et al. 2004). During the experiments, water samples were taken from the treated and control units before the treatment and after the treatment for 4 (**I**) to 6 (**II**) h.

2.5 Setup of the macrophyte study (III)

The effect of macrophytes on nutrient dynamics was studied at Lake Kirkkojärvi at two different macrophyte (submerged SUB and floating-leaved FLOAT) stations and at one open-water (OPEN) station (station area 400 m^2, six sampling points at each station) (Fig. 1). The macrophyte stations were among submerged (whorled water-milfoil *Myriophyllum verticillatum* L.) and floating-leaved (yellow water-lily *Nuphar lutea* (L.) Sm.) macrophytes. The water depths at the stations were 0.7 m at SUB, 1.2 m at FLOAT and 1.7 m at OPEN. The changes in the nutrient concentrations at the stations were measured throughout the open-water season in 2010 (April–

November) at 2-wk sampling intervals. The development of the macrophyte stands and the changes in the chlorophyll *a* concentration were also monitored. Macrophyte growth was monitored by calculating the stem density of floating-leaved macrophytes and percentage of volume infested (PVI) (Schriver et al. 1995) of the submerged macrophytes.

2.6 Setup of the O_2 study (IV)

The effects of O_2 availability on nutrient dynamics were studied at four stations in the Enonselkä basin of Lake Vesijärvi (Fig. 1). The stations represented four different treatments from shallow and continuously oxic area ST1 to deeps where O_2 is depleted during summer stratification (Table 1). Two of the study deeps were artificially aerated with Mixox units (Mixox MC-1100; Water-Eco Ltd, Kuopio, Finland). The Mixox devices pump epilimnetic water through the thermocline into the hypolimnion and preserve thermal stratification. At ST2, the aeration was operated continuously throughout the thermal stratification period and at ST3 the aeration was conducted in three pulses that lasted for 15–20 d. The aeration was stopped for 7 d and 36 d between the three aeration pulses. At ST4 no aeration was used.

Table 1. Treatments at each study station in the Enonselkä basin (**IV**).

Station	Location	Depth (m)	Treatment
ST1	Ruoriniemi	5	Oxic
ST2	Lankiluoto	33	Continuous aeration
ST3	Vasikkasaari	17	Pulsed aeration
ST4	Paimelanlahti	14	No aeration

2.7 Statistical analyses

The effects of treatments were tested with analysis of variances for repeated measures (rANOVA), which accounts for autocorrelation between sequential samples (SAS Institute 1990) (**I–IV**). The linear regressions between the added concentration of $^{15}NO_x^-$-N and D_{14} or D_{15} were tested with regression analyses (**II, IV**). The linear regressions between D_{14} or D_{15} and LOI, temperature, concentrations of O_2 and ambient NO_x^--N were tested, as well as regressions between D_n or denitrification based on overlying water NO_x^--N (D_w) and concentration of NO_x^--N (**IV**).

3 RESULTS

3.1 Effect of resuspension on nutrient dynamics (I, II)

During the resuspension treatments, the concentration of SS increased from 10–60 mg l^{-1} to levels of 160–390 mg l^{-1}. During the first 20 min after treatment, the concentration decreased rapidly. During the rest of the experiment (4–6 h), the SS continued to decrease but remained higher than the initial level (**I, II**). Both the concentration of TN and TP also increased markedly during the treatments, TN by > 500 µg l^{-1} and TP by > 200 µg l^{-1} (Fig. 4) (**II**). However, the TN:TP ratio decreased during resuspension, regardless of the phase of the growing season, due to the relatively smaller increase in the concentration of TN (Fig. 4) (**II**).

Both in 2006 and 2009, the resuspension treatment significantly increased the concentration of SRP in May and August (Fig. 5) (**I, II**). The concentration of NO_x^--N also increased in May and August, but decreased in November (Fig. 6) (**II**). Then again, the concentration of NH_4^+-N increased in August and November (Fig. 6) (**II**). However, except for SRP in May 2006, the changes in dissolved nutrients were less than 10 µg l^{-1}. The concentration of O_2 in the water was between 7.2 and 12.1 mg l^{-1} during all of the experiments (Table 2) (**I, II**). In 2006, the water pH increased from 7.5 in May to 9.3 in August, but in 2009 the pH remained near-neutral (7.3–7.8) during all of the experiments (Table 2) (**II**).

The LOI of the surface sediment at the location of the resuspension experiments in Lake Kirkkojärvi was between 10% and 12% throughout the open-water season in 2006 and 2009 (Table 2). The fractionation of P content of the sediment showed that the Ca-P constituted 63–75%, Fe-P 19–29%, Al-P 5–8% and the fraction of labile P 1% of the total fractionable P (TFP), which was 480–510 mg kg^{-1}.

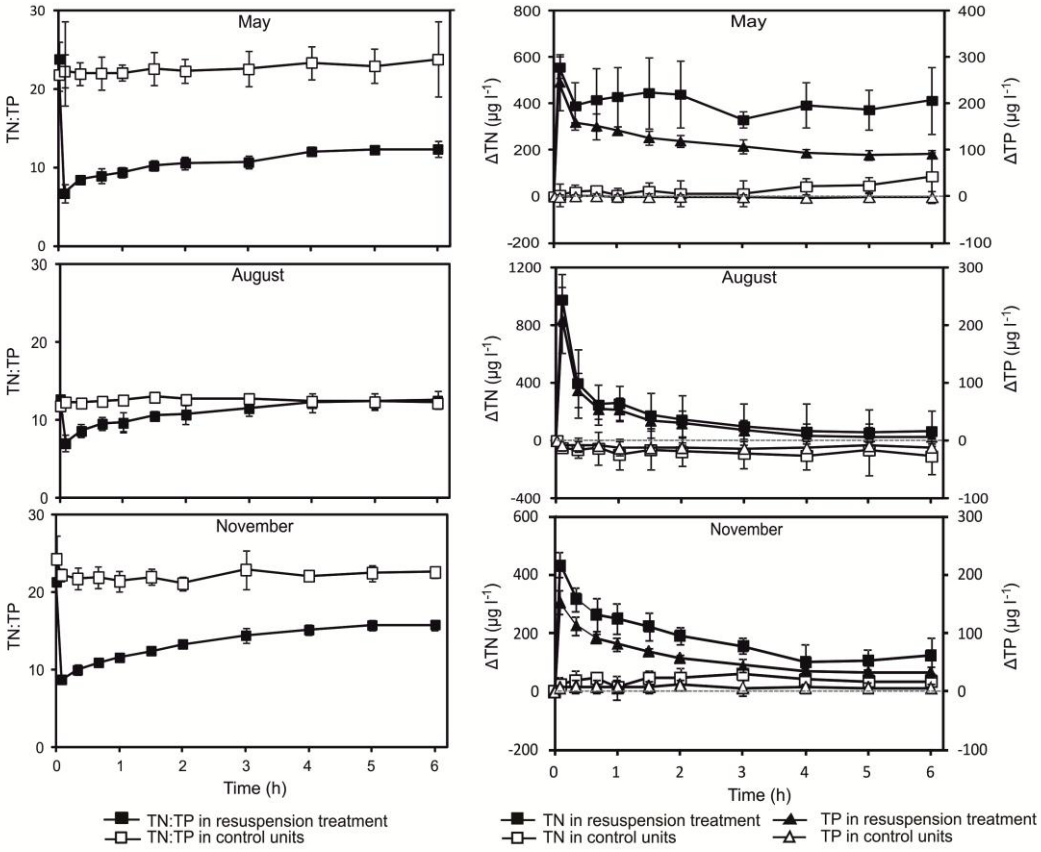

Figure 4. Changes in the TN:TP ratio, TN and TP concentrations during the resuspension experiments in 2009 (± 95% confidence limits). Note the different scales on the y-axes. Modified from article **II**.

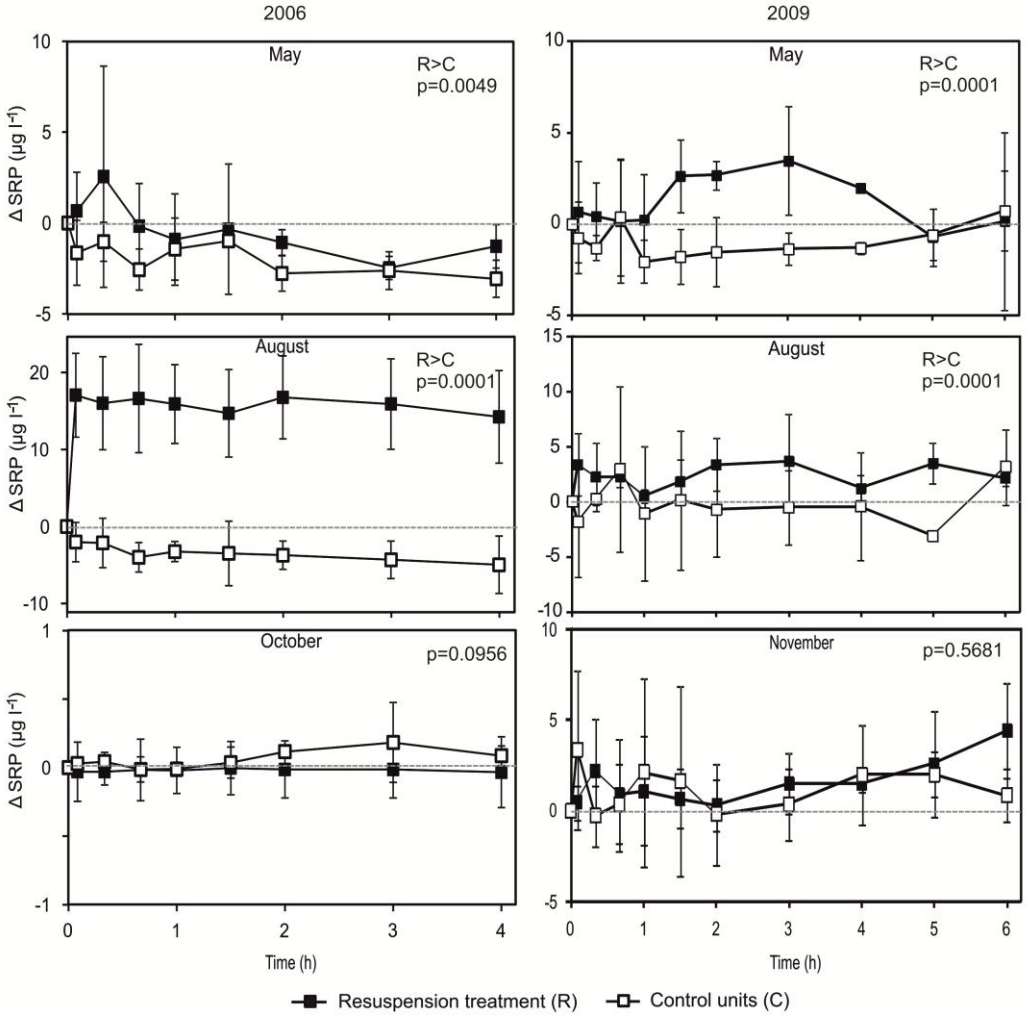

Figure 5. Changes in the concentration of SRP during the resuspension experiments in 2006 and 2009 (± 95% confidence limits). Note the different scales on the y-axes. Modified from articles **I** and **II**.

Table 2. Water-quality parameters, growth of macrophytes, loss on ignition (LOI) of surface sediment, denitrification rate (D_{14}) and denitrification potential (D_{15}) at study lakes in 2006–2011. The average values in spring, summer and autumn are presented. See original publications for sampling dates.

		Lake Kirkkojärvi					Enonselkä basin			
		2006 (**I**)	2009 (**II**)	2010 (**III**)			2011 (**IV**)			
				SUB	FLOAT	OPEN	ST1	ST2	ST3	ST4
Temperature	Spring	13.3	11.9	14.1	14.8	14.0	10.7	8.2	-	4.9
(°C)	Summer	20.0	20.5	18.1	19.0	19.1	18.9	16.7	16.4	10.9
	Autumn	10.7	0.8	-	-	2.6	11.6	11.8	11.6	11.2
pH	Spring	7.5	7.5	6.6	7.1	7.1	7.7	7.6	-	7.7
	Summer	9.3	7.3	6.8	7.2	7.5	7.7	7.4	7.5	7.3
	Autumn	7.8	7.8	-	-	8.5	7.8	7.8	7.8	7.7
DO	Spring	11.1	9.8	4.4	8.5	8.3	11.0	8.7	-	6.4
(mg l^{-1})	Summer	7.2	7.9	3.5	7.4	8.4	6.6	0.1	0.1	0.3
	Autumn	8.1	12.1	-	-	11.2	10.3	9.8	10.1	10.1
Chlorophyll *a*	Spring	11	18	46	22	12	-	-	-	-
(µg l^{-1})	Summer	122	20	13	15	19	-	-	-	-
	Autumn	28	2	14	9	12	-	-	-	-
LOI	Spring	11	10	27	13	9	11	13	-	15
(%)	Summer	12	12	26	14	11	11	14	14	13
	Autumn	12	11	31	15	12	12	12	13	13
PVI / density	Spring	-	-	1	1	-	-	-	-	-
(%) / (stems m^{-2})	Summer	-	-	75	15	-	-	-	-	-
	Autumn	-	-	48	13	-	-	-	-	-
D14	Spring	-	5.81	2.43	2.52	0.71	2.01	3.30	-	28.71
(mg N m^{-2} d^{-1})	Summer	-	3.02	1.42	3.29	1.62	3.32	2.06	1.74	2.94
	Autumn	-	3.04	0.88	3.27	2.99	2.99	1.51	3.12	3.37
D15	Spring	-	3	-	-	-	4	11	-	33
(slope)	Summer	-	21	-	-	-	13	8	14	8
	Autumn	-	5	-	-	-	4	8	8	29

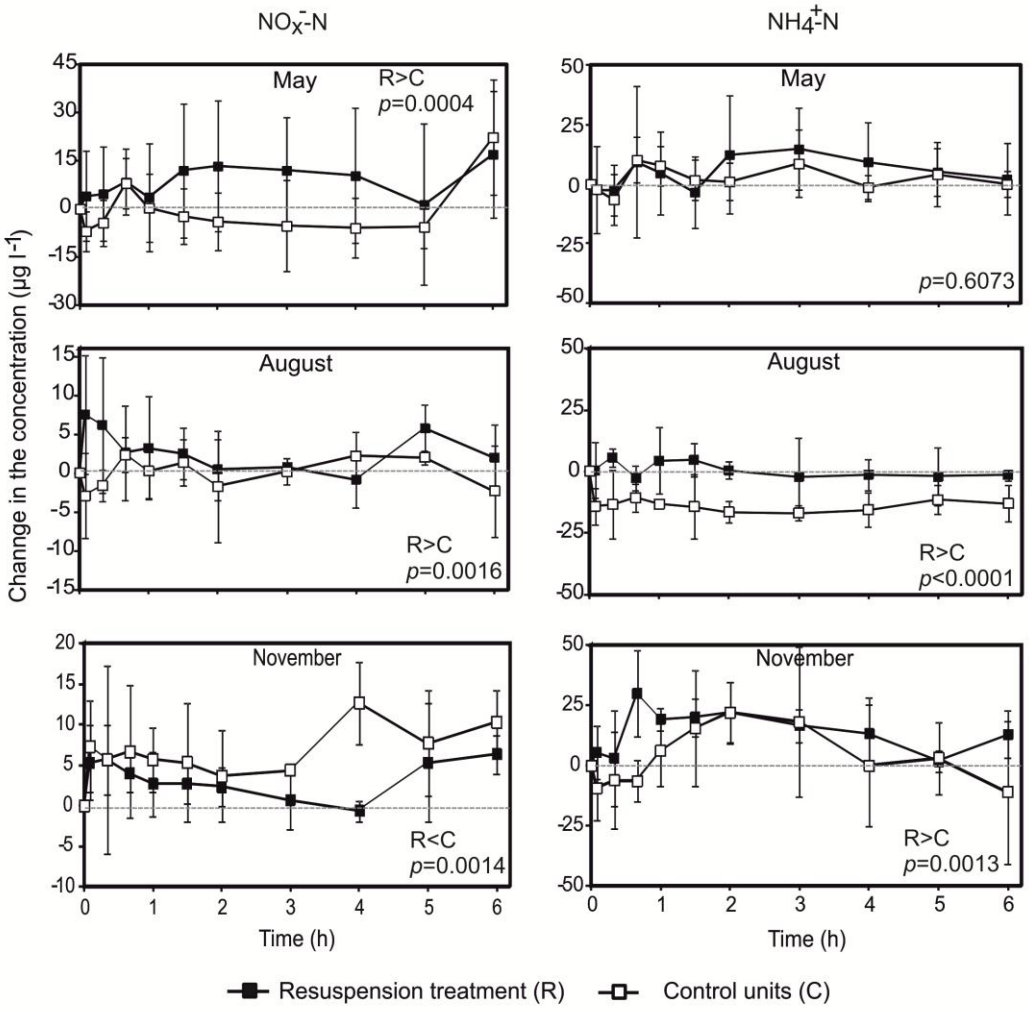

Figure 6. Changes in the concentration of DIN during the resuspension experiments in 2009 (± 95% confidence limits). Note the different scales on the y-axes. Modified from article **II**.

3.2 Effect of macrophytes on nutrient dynamics (II, III)

The PVI and density of the macrophyte stands increased during summer. In August, the highest PVI at the SUB station was 75% and the highest density at FLOAT 15 stems per m^2 (Table 2) (**III**). The concentration of O_2 was constantly lower ($p < 0.01$) at the SUB station (0.6–8.1 mg l^{-1}) than at the FLOAT or OPEN stations (5.6–11.2 mg l^{-1}). The LOI of the surface sediment was highest at SUB (26–31%) and lowest at OPEN (9–12%) (Table 2) (**III**). The penetration of O_2 was deeper (2.3–6.3 mm) at the OPEN station sediments than at the macrophyte stations (1.2–4.8 mm), and at all of the stations the O_2 penetration depth increased from August to November (**III**). The porosity of the sediment was highest at SUB (93–94%) and lowest at OPEN (87–90%).

During the sampling period in 2010, the concentration of NO_x^--N varied widely between the various stations. In early summer and in autumn, the concentration was significantly lower at SUB that at FLOAT or OPEN. In June the concentration dropped steeply and in late summer NO_x^--N was depleted at every station (**III**). In 2009 during the resuspension experiments in the open water, the concentration of NO_x^--N also decreased from 670 µg l^{-1} in May to the detection limit (< 2 µg l^{-1}) in August and increased to 590 µg l^{-1} in November (**II**). The concentration of NH_4^+-N did not show such clear differences between the stations or over time. The concentration of NH_4^+-N varied between 10 and 100 µg l^{-1} during the summer months (May–August) and increased to 100–150 µg l^{-1} between September and November (**II, III**). With regard to NH_4^+-N, the SUB station also differed significantly from the other stations (**III**). The concentration of SRP was similar at FLOAT and OPEN (10–23 µg l^{-1}), but significantly lower (5–14 µg l^{-1}) at SUB. The concentration of TP, however, was highest at SUB (on average 95 µg l^{-1}) and lower at FLOAT and OPEN (on average 73 µg l^{-1}) (**III**). The concentration of TN at SUB differed significantly from that at the other stations, except for one measurement (12th July) (**III**). In early summer, TN was lower at SUB, but higher in late summer (**III**).

In 2009, the highest D_{14} value, 5.81 mg N m^{-2} d^{-1}, was already measured in May and the lowest rate in August (**II**). In 2010 the highest rate (11.4 mg N m^{-2} d^{-1}) was measured at the OPEN station in late June and lowest at OPEN and SUB (0.7 and 0.9 mg N m^{-2} d^{-1}) in April and November, respectively (Fig. 7) (**III**). Overall, the average D_{14} was significantly ($p < 0.01$) lower at SUB (1.48 mg N m^{-2} d^{-1}) than at FLOAT (4.29 mg N m^{-2} d^{-1}) or OPEN (4.19 mg N m^{-2} d^{-1}) (**III**). The denitrification potential, D_{15}, was seasonally measured in 2009 at Lake Kirkkojärvi. D_{15} increased from 3 in May to 21 in August and decreased back to 5 in November with decreasing temperature (**II**).

3.3 Effect of O_2 availability on nutrient dynamics (I–IV)

The studies at Lake Kirkkojärvi (**I–III**) represented conditions under which O_2 is continuously available. In the Enonselkä basin, study deeps ST2 and ST3 were artificially aerated, but even the continuous aeration at ST2 was not sufficient to prevent anoxia during summer (**IV**). However, aeration postponed the beginning of anoxia and even during the anoxia promoted nitrification: at ST3 aeration pulses increased the concentration of NO_x^--N, whereas during the pauses the concentration of NO_x^--N decreased, while the concentration of NH_4^+-N increased (Fig. 7) (**IV**).

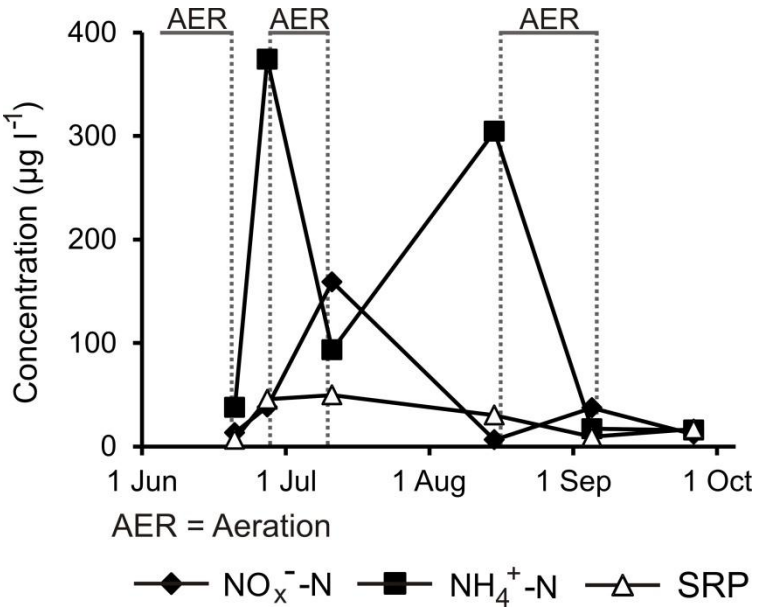

Figure 7. Effect of aeration on nutrient dynamics at ST3 in the Enonselkä basin (95% confidence limits ± 0.3–3.9 at every point) (**IV**).

In the unaerated deep, NH_4^+-N accumulated in the water during summer and its concentration decreased only after the autumn turnover. At the other stations, the concentration of NH_4^+-N was also usually higher than the concentration of NO_x^--N (**IV**). During the stratification, the SRP concentration increased at every deep station and did not decrease back to the initial level during the stratification. The highest SRP concentration (113 µg l^{-1}) was measured at ST4 in August (**IV**).

The D_{14} value in the Enonselkä basin was highest (28.71 mg N m^{-2} d^{-1}) in May at ST4 and lowest (1.32 mg N m^{-2} d^{-1}) in July at the same station (**IV**). The D_{14} value at ST4 differed significantly from that of the other stations ($p < 0.001$), but no differences in D_{14} between stations ST1–ST3 were found. Both at Enonselkä and at Kirkkojärvi, D_{14} was strongly affected by the concentration of NO_x^--N in the water (Fig. 8). The high peak in the concentration of NO_x^--N at ST4 in May was reflected in a high D_{14} value. At ST3, the D14 value decreased by half during the aeration pauses and

consequential decrease in NO_x^--N. The D_{15} values varied between 2 and 33 and no dependence ($p > 0.05$) between D_{15} and NO_x^--N, O_2 or temperature was found (**IV**).

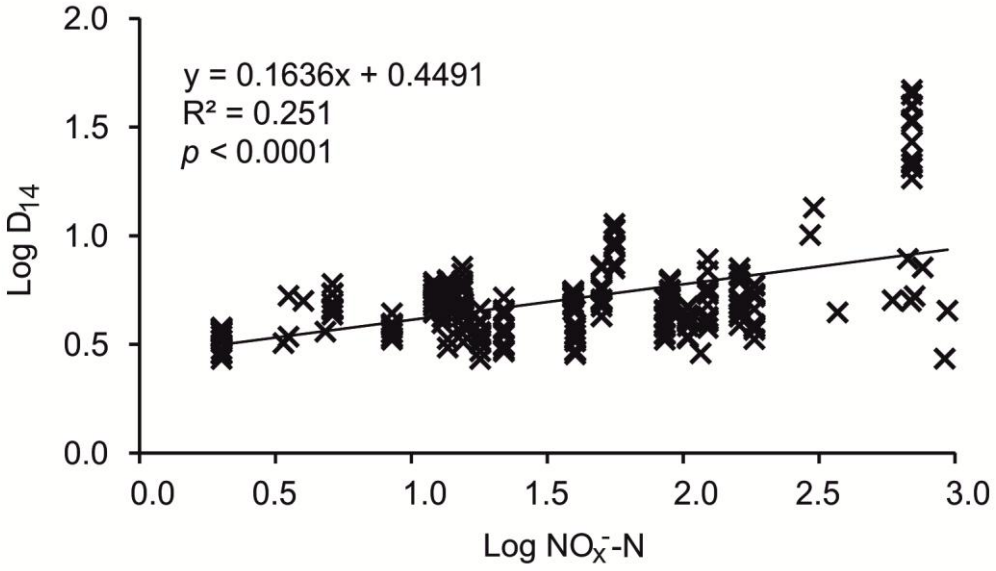

Figure 8. Rate of denitrification (D_{14}) at various concentrations of NO_x^--N. Pooled data of studies at Lake Kirkkojärvi (years 2009 and 2010) and in the Enonselkä basin (year 2011). All data are log-transformed.

4 DISCUSSION

4.1 Effect of resuspension

The resuspension treatments increased the total nutrient concentrations in water significantly. The resuspension rate is regulated, among other things, by the sediment's critical shear stress, which may vary seasonally due to changes in the sediment's composition. During the growing season, organic material settles and this newly sedimented material is less compact and more easily resuspended (Bengtsson & Hellström 1992, Weyhenmeyer 1998). This may lead to changes in the intensity of resuspension and in the TN:TP ratio of water during summer (Niemistö et al. 2008). In the present studies, the resuspension induced was strong enough to exceed the sediment's critical shear stress throughout the open-water season. The increase in concentration of SS of the water corresponded to resuspension of 0.3–0.5 cm of the surface sediment. Although the concentration of SS peaked substantially in the columns treated, the peak already declined after 20 min, due to rapid sedimentation of the heaviest resuspended particles. The concentration of TP followed the concentration of SS in all experiments, as was also found by Kristensen et al. (1992) and Søndergaard et al. (1992). The concentration of TN increased in every experiment, but due to the relatively larger increase in the concentration of TP the TN:TP ratio decreased, regardless of the season.

Although the TN:TP ratio describes the changes in nutrient availability in a lake, the actual changes in the concentrations of readily available nutrient forms (SRP and DIN) provide more detailed information on the nutrient dynamics. Both in 2006 and in 2009, the concentration of SRP increased, due to the resuspension treatment in May and August. Often the aerobic release of P is associated with specific ligand-exchange reactions that occur on the surface of the Fe or Al oxides. The ligand-exchange reactions are strongly affected by the prevailing pH (Andersen 1975, Zhou et al. 2005, Christophoridis & Fytianos 2006). This is especially important in eutrophic lakes, where intense primary production may elevate the pH and thereby enhance P release (Drake & Heaney 1987, Boström et al. 1988a). The effect of high pH was observed in Lake Kirkkojärvi in August 2006. At that time, the water pH (9.2) was at the level where the highest P release occurs (Andersen 1975). In August 2009, resuspension also significantly increased the concentration of SRP, but this increase was smaller. The water pH (7.3) at the time was near-neutral and at such pH the P release remains lower compared with that at higher pH levels (Van Hullebusch et al. 2003, Christophoridis & Fytianos 2006). In May, the SRP also increased significantly, but the actual increase was very small (< 5 μg l^{-1}).

The results from the fractionation of TFP also support the conclusion of ligand-exchange reactions as 24–37% of the TFP was in fractions of Al-P and Fe P that are susceptible to such reactions. The TP concentration (determined with an inductively coupled plasma (ICP) mass spectrometer after wet combustion with nitric acid and hydrogen peroxide) in the sediments of Lake Kirkkojärvi varied between 1.1 and 1.3 mg g^{-1} (Niemistö et al. 2009), while the TFP was 0.5 mg g^{-1}. Thus, the TP is not equivalent to TFP. The fractionation, however, provides information on the various P pools in sediment and improves the ability to assess under which conditions P would be released from the sediments.

The effects of resuspension on P and N are different. As a cation, NH_4^+-N is able to bind to negatively charged sediment particles and can therefore be involved in adsorption-desorption reactions (Rosenfeld 1979, Seitzinger et al. 1991). Most of the increase in NH_4^+-N concentration after resuspension may be due to desorption from the resuspended particles rather than from the porewater (Morin & Morse 1999). The release of NH_4^+-N can therefore be noticeable, especially in shallow areas (Rizzo & Christian 1996, Sloth et al. 1996). NO_x^--N, however, is not able to bind to sediment and the direct effect of resuspension on NO_x^--N is restricted to transport of porewater to the lake water. However, resuspension should be substantial before resuspended porewater N would significantly affect the N concentration in the water (Blackburn 1997), since both the N concentration in porewater and the volume of resuspendable sediment are so limited. Possibly, the changes observed in NO_x^--N were rather related to mineralization of resuspended organic N during the experiment.

4.2 Effect of macrophytes

At Lake Kirkkojärvi, the stands of submerged macrophytes provided shelter against resuspension, although the water depth was lower than at the other stations. The concentration of TP at the SUB station was highest among the stations in early spring. As the plant coverage at SUB increased, the sheltering effect of plant beds against resuspension was enhanced and the differences in TP between the stations declined. Such effect of macrophytes on resuspension was also previously described at Lake Kirkkojärvi (Horppila & Nurminen 2003).

The N concentration in water was significantly lower at the SUB station than at FLOAT or OPEN. The various uptake mechanisms of submerged and floating-leaved plants explain the differences among the macrophyte stations, since *Nuphar* takes nutrients from the sediments while *Myriophyllum* is able to use nutrients directly from the water (Best & Mantai 1978, Ciurli et al. 2009). Additionally, the water depth at the SUB station, was lower, which led to a higher NO_x^--N depletion rate per volume of water than at the FLOAT station.

In addition to macrophytes and phytoplankton, denitrifying bacteria also compete for N. The biomass and density of macrophytes enhance denitrification (Saunders & Kalff 2001). However, at FLOAT and OPEN the organic content of the sediments was so similar that differences in the D_{14} values due to organic C availability were unlikely. At SUB, the LOI was twice as high as at the other stations, but the D_{14} value remained lowest. This can be due to the organic-rich environment, where the availability of NO_x^--N rather than organic C regulates denitrification (Forshay & Dodson 2011). At Lake Kirkkojärvi in 2010, the highest rates of denitrification were measured at OPEN and FLOAT in late June. By that time, the availability of NO_x^--N at SUB was so low that it limited denitrification. Due to the low availability of NO_x^--N, the highest D_{14} value at SUB were already measured in April. In August, denitrification was restricted by the availability of NO_x^--N at all of the stations.

Overall, the effect of macrophytes, especially submerged species, on N dynamics was significant. Among submerged macrophytes NO_x^--N was depleted more rapidly than among floating-leaved plants or in the open water. This also restricted the D_{14} value, which was slowest at the SUB station.

4.3 Effect of O_2 availability

O_2 conditions in the sediment are crucial to determining N dynamics. Macrophytes affect the O_2 conditions in the sediment by transporting O_2 through their roots and creating oxic microenvironments in the anoxic parts of the sediment. However, among macrophytes the high organic content of the sediment and increased mineralization may also decrease O_2 penetration (Caffrey et al. 1993). This was seen at Lake Kirkkojärvi, where O_2 penetrated deeper in the sediments of open-water areas than at the macrophyte stations. The O_2 penetration depth is also affected by the porosity of the sediment (Cai & Sayles 1996). The diffusion of O_2 into the sediment is faster when the porosity is high. Thereby, it appears unlikely that the O_2 penetration was deeper at the OPEN sediments due to physical sediment quality, since the porosity at the OPEN sediments was lower than at SUB or FLOAT. Rather, the content of organic material and O_2 consumption in the sediment was lower outside the macrophyte stands, and in addition resuspension was able to effectively aerate the bottom. In deeper stratifying areas, however, the effect of resuspension in aerating the sediment would be negligible.

In the Enonselkä basin, the effect of O_2 availability was seen in the shallow area and also during aeration in the deep basins. Accumulation of NH_4^+-N and SRP did not occur and in the aerated basins NO_x^--N remained available, although the aeration effort was not sufficient to maintain the water in an oxic state during summer. The pulsed aeration induced impressive alternation in the concentrations of NO_x^--N and NH_4^+-N. The

concentrations, especially of NH_4^+-N, showed contrasting trends, decreasing and increasing dramatically during and after the aeration periods. Such effects of O_2 pulses and pauses were previously obtained in laboratory experiments (Beutel et al. 2007), but treatment at ST3 showed that similar effects also occurred on the lake scale. In the unaerated deep, accumulation of NH_4^+-N was observed in late summer.

Aeration increases the temperature of hypolimnetic water and thereby enhances mineralization and O_2 consumption. Both chemical and microbial processes compete for O_2 (Sweerts et al. 1991, Brune et al. 2000, Bryant et al. 2012), and oxidation of reduced substances that have accumulated during anoxia buffers against recovery of O_2 conditions in the water (Conley *et al.* 2009, Middelburg & Levin 2009). The capacity of the aerators used in the Enonselkä basin was not sufficient to maintain oxic conditions in the hypolimnion. The pulsed aeration was especially insufficient, due to the slow recovery of O_2 conditions after even a short pause in aeration (Bryant *et al.* 2011). However, the aeration used was able to maintain nitrification, even though the concentration of O_2 was below the detection limit.

4.4 Role of denitrification in eutrophic lakes

NO_x^--N is the substrate for denitrification and thereby resuspension; macrophytes as well as O_2 availability may affect the rate of denitrification. Seasonally, the changes in concentration of NO_x^--N and in temperature were the main factors regulating denitrification in Lake Kirkkojärvi. Rising temperatures enhance denitrification (van Luijn et al. 1999) and the effect of temperature was seen in the denitrification potentials in Lake Kirkkojärvi. Temperature was also the most important factor in regulating denitrification in late autumn in Lake Kirkkojärvi, when denitrification remained low, regardless of the substantial NO_x^--N availability. In summer, however, the rate of denitrification remained lower than would be expected, based on temperature only, due to the limited availability of NO_x^--N. The dependence between denitrification and water NO_x^--N concentration has frequently been recorded (Risgaard-Petersen & Ottosen 2000, Maerki et al. 2009, McCrackin & Elser 2010, Deek et al. 2012), and the pooled data of D_{14} at various NO_x^--N concentrations in Lake Kirkkojärvi and in the Enonselkä basin also showed significant regression.

In neither lake was anammox detected. This result is in line with a recent study in Finland, in which no anammox activity was detected in four boreal lakes (Rissanen 2012). Probably, the lake environment was not favourable for anammox bacteria, due to the continual changes in conditions. The possibility of DNRA competing effectively with denitrification for NO_x^--N also appears unlikely with regard to the literature, since the C:N ratio and temperature were not especially high and no hydrogen sulphide was observed (Daalsgaard & Thamdrup 2002, Nizzoli et al. 2010, Jäntti &

Hietanen 2012). However, even though the denitrification potentials were high, denitrification was responsible only for 10% of the decrease in NO_x^--N during the aeration pause at ST3. The calculations were based on the D_{14} value and the change in mass of NO_x^--N in the hypolimnion. The rest of the decline in the concentration could be attributed to the DNRA process, since primary production does not contribute to uptake in the hypolimnion, and accumulation of NH_4^+-N was significant. Possibly, the aeration did not affect the rate of DNRA, but during the aeration pulses DNRA was coupled with nitrification, which directly oxidized NH_4^+-N and prevented accumulation. In addition to DNRA, NO_3^--dependent Fe(II) oxidation could be responsible for producing NH_4^+-N during aeration pauses (Weber *et al.* 2006, Coby *et al.* 2011). Both of these processes cycle available N in the lake ecosystem and do not produce N_2 and cause N removal. N_2 removal by denitrification was calculated to be highest in the deep with continuous aeration and lowest in the unaerated deep. In Lake Kirkkojärvi, D_{14} values were slowest in sediments of the submerged macrophytes. In both of the study lakes, the availability of NO_x^--N showed the strongest influence on denitrification during summer when the temperature was favourable.

5 CONCLUSIONS

This thesis shows that in a shallow lake, the effect of resuspension on P release is dependent on the conditions prevailing in the lake water. Elevated pH in water induced aerobic P release and the effect of resuspension varied seasonally. The effect of resuspension on DIN was not as clear, but resuspension also increased the concentrations of NO_x^--N and NH_4^+-N during some of the experiments. Furthermore, strong resuspension decreased the TN:TP ratio independently of the phase of the open-water season. These experiments emphasize that in shallow lakes, resuspension significantly affects nutrient cycles by transporting the material to the lake water.

The concentrations of dissolved nutrients in the water were strongly affected by both the macrophytes and availability of O_2. Among submerged macrophytes, the concentrations of dissolved nutrients were, in general, lower than among floating-leaved plants or in open water. The D_{14} values were also lower in sediments among the submerged plants. The possible positive effects of macrophytes on denitrification were masked by the low availability of NO_x^--N among the submerged macrophytes.

The effect of artificial aeration on the dynamics of NO_x^--N and NH_4^+-N was clear, since the concentrations of NO_x^--N and NH_4^+-N fluctuated in opposite directions during the aeration pulses and pauses. SRP accumulated in the unaerated deep during stratification, but did not increase during the aeration pauses in the deep with pulsed aeration. Even though the effect of aeration was not sufficient to maintain the hypolimnion in an oxic state, it did maintain levels of NO_x^--N available in the water.

In both of the lakes, the D_{14} value was mainly dependent on the availability of NO_x^--N and on the temperature. Since denitrification removes N from the water and not only from the sediment prone to resuspension, it also directly affects the water TN:TP ratio as well as nutrient dynamics of shallow lakes. In the deeper areas, the effect of denitrification on N concentrations was lower and DNRA may also have contributed to NO_x^--N reduction. The temperature of the hypolimnion increased in both artificially aerated deeps, but aeration pauses restricted the warming by several degrees. However, during the aeration pauses the denitrification decreased and NH_4^+-N concentration increased. It can be concluded that the pulsed aeration was not sufficient to maintain the water in an oxic state or enhance favourable nutrient cycling. Even the use of continuous aeration may result in problems, since the O_2 consumption increases with increasing temperature and thereby decreases the hoped-for effects.

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